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(54) Title: CERAMIC COMPOSITIONS			
(57) Abstract <p>A ceramic material useful in the fabrication of durable aesthetic heat pressed dental restorations is disclosed. The ceramic has a high flexural strength characteristic, preferably provided by a uniform microstructure caused by the dispersion of crystals during heat pressing. Preferably, the crystals used in the ceramic are leucite and are oriented similarly throughout the ceramic. Even more preferably, an ideal crystalline content is employed such that the ceramic has increased flow at lower processing temperatures, thereby increasing the fit and aesthetics of the finished ceramic restoration.</p>			

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CERAMIC COMPOSITIONS

This nonprovisional application depends from provisional application number 60/120,967, filed February 19, 1999.

Technical Field

This invention relates to ceramic compositions of increased strength and methods of making these compositions. The compositions generally include a uniformly dispersed crystalline material that contributes to increased strength and durability.

Background

Ceramics have been previously evaluated and shown to contain microstructural defects, which may degrade their flexural strength and durability. Microcracking associated with larger leucite crystal sizes or agglomerates and the susceptibility of the glassy matrix to fracture are potential strength limiting factors.

Ceramic powder frit materials have many applications in dentistry. They may be applied to metal substructures, high strength cores and into and onto refractory casts, in order to make aesthetic ceramic restorations. While not without merit, the strength of these materials is never fully achieved as individual building and firing techniques always leave a distribution of flaws, voids and porosities. Firing shrinkage of the powder compact also necessitates multiple firing schedules to produce the required tooth contour and accuracy of marginal fit necessary for a dental restoration. Hot pressing is a processing method which has been used for industrial ceramics and both dental porcelain fused to metal and ceramic restorations.

The IPS Empress systemTM utilized custom made leucite-containing ceramic ingots for the hot pressing technique. This has been followed by the OptimalTM pressable ceramic system. This system involves the investing of an accurate wax up in a refractory mold, which is burnt out to allow a preheated leucite-containing ceramic to be pressed into it, via a plunger under pressure from a pneumatic press furnace. The ceramic ingots are available in several different shades and transparencies including vita dentine shades, color translucent and translucent types, to suit the required clinical situation. Restorations may be completed on a

1 color matched die by the application of stains and glazes or alternatively cut back and veneered
2 with thermally compatible porcelains prior to glazing. Since wax fabrication techniques can be
3 used in conjunction with this technique it is possible to achieve good marginal adaptation and
4 accurate occlusal restoration relationships with ease. The illumination of opaque alumina or
5 metal substructures means that excellent aesthetics can be achieved and the problem of
6 matching crowns to veneers is technically solved with ease. These restorations also benefit
7 from adhesive bonding to etched tooth structure, which is thought to increase their overall
8 strength. The overall factors being associated with: (1) reduction of ceramic surface flaws by
9 the resin and the creation of surface compression by the polymerization shrinkage of composite
10 luting cements and (2) the ability of the composite lute to act as a shock absorber and transfer
11 the occlusal load to the supporting tooth structure.

12 Pressable ceramic systems have been fairly successful when placed in the correct
13 clinical stress situation, however, *In vitro* studies suggest that microstructural defects exist in
14 these ceramic materials which may degrade their strength and durability, see Cattell, *The*
15 *transverse strength, reliability and microstructural features of four dental ceramics - part*
16 *1*, J. Dent. 25:399-407 (1997). Previously microcracking associated with large leucite crystal
17 sizes or agglomerates and the susceptibility of the glassy matrix to fracture due to the lack of
18 a uniform leucite crystal distribution have been cited as potential problems, Cattell, *The Biaxial*
19 *Flexural Strength of Two Pressable Ceramic Systems*. J. Dent. (1998). The critical leucite
20 crystal size, content or distribution had not been optimized in these material in order to
21 maximize their strength properties. A high-strength ceramic is very useful in dental restorations,
22 as well as other applications.

23 Leucite content in borosilicate and feldspar glasses above 20% wt results in reductions
24 in bending strength, which is explained by the large mismatch of thermal expansion and the
25 degree of microcracking which was not present in compositions with smaller additions of
26 leucite. Glass compositions with a large amount of Na and lower deformation temperature,
27 however, show increases in strength with leucite addition due to probable increases in the
28 expansion coefficient of the glass and reduction in the residual stresses during cooling. Simply

1 increasing the volume fraction of leucite into the glassy matrix may therefore not be solely
2 responsible for increasing strength in these systems. Leucite distribution, crystal size and the
3 composition of the glassy matrix must all be considered.
4

5 **Summary of the Invention**

6 The present invention relates to a ceramic material with an ideal microstructure and a
7 process of using hot pressing in order to increase its mechanical properties and ease of use.
8 The end result is a ceramic material with properties that make it very effective for use in
9 producing dental restorations, especially those restorations using the staining technique.

10 More particularly, the invention relates to a heat pressable ceramic material having high
11 mean flexural biaxial strength. Fine leucite crystals evenly distributed throughout a glassy matrix
12 provide ideal strength properties for ceramic material. A ceramic material with an ideal
13 microstructure, processed using hot pressing techniques, has the desired increased flexural
14 strength and ease of use. The fine leucite crystal size together with the uniformity of
15 microstructure caused by the dispersion of the leucite crystals throughout the material, and their
16 arrangement in a uniform orientation significantly increases the ceramic's strength. This is
17 demonstrated by the significant improvements in biaxial flexural strength observed in ceramics
18 produced through the processes disclosed. Optimization of the microstructure by producing
19 a fine microstructure and controlling its distribution via the correct pressing parameters is
20 extremely advantageous in these systems.

21 These processes can be used with commercially available press furnaces using existing
22 equipment without a statistical difference in biaxial flexural strengths. The ceramic may have
23 a degree of damage tolerance or more probably the firing cycles may eliminate surface flaws.
24

25 **Disclosure of the Invention**

26 In certain embodiments of the present invention, the heat pressed ceramic materials
27 have a completely homogeneous particle distribution which eliminates any large glassy areas
28 and distributes the leucite particles in a gap grading effect. It is believed that preferred crystal

1 orientation and the easier movement of the fine leucite crystals ($1.2 \pm 1.1 \mu\text{m}^2$) through a low
2 viscosity glass might account for these phenomena.

3 Certain embodiments of the present invention include ceramics with a fine leucite crystal
4 size that are well-bonded and devoid of any significant matrix microcracking. Heat pressing
5 of frit material increases its strength by orienting the crystals contained therein and providing for
6 their uniform distribution. A uniformity of microstructure indicates that the fine leucite crystals
7 and resultant stresses are evenly distributed throughout the glassy matrix, making crack
8 diversion or blunting more probable. The presence of large particle inclusions of particle
9 agglomerates above a critical size is associated with extensive microcracking in the glassy
10 matrix, thereby producing stress raisers larger than the inherent flaws, as the energy for a
11 growing flaw is potentially provided by the elastic stored energy in the particle and adjacent
12 glassy matrix. It is believed that changes in leucite volume fraction during porcelain firing cycles
13 contributes to residual stresses in the porcelain and affects the microcrack density.

14 Lower levels of leucite used in the heat pressed ceramic provided significantly higher
15 biaxial flexural strengths than heat pressed leucite ceramics presently used, which in some cases
16 contain double the leucite volume fraction of the preferred embodiments. In fact, it is believed
17 there is no significant linear relationship between increasing additions of leucite and higher mean
18 biaxial flexural strength values.

19 The base glass produces an opalescent colored material but secondary electron imaging
20 did not ascertain whether this was due to glass phase separation or the presence of titanium
21 dioxide nucleating agents. The formation of compounds by combining titanium dioxide with
22 other oxides allows ease of nucleation with prior glass phase separation. The attainment of
23 fine-grained microstructures is enhanced by prior glass phase separation with the mechanical
24 interference reduction in nuclei growth. The nucleation and growth of leucite crystals in the
25 ceramic is associated with a surface crystallization process as the heat treatment of glass
26 monoliths following the melting of the glass components does not result in the controlled
27 nucleation and growth of leucite crystals. Alteration of the powder size before heat treatment

1 directly effects the size and distribution of the crystalline phases precipitated. The surfaces of
2 small particles can be used to initiate the crystallization of bulk specimens.

3 X-ray diffraction showed the presence of tetragonal leucite and an amorphous
4 component in the ceramic and distinctive tetragonal leucite twinning was clearly visible in the
5 microstructure. It is believed that lamellar and merohedric twinning in natural leucite is caused
6 by the change encountered during cubic to tetragonal phase transformation. Twinning of
7 tetragonal leucite and the presence of tangential compressive stresses around the crystals are
8 thought to be important factors in the fracture resistance of these materials. The crystallization
9 and retention of cubic leucite does not provide the degree of residual tangential stresses or
10 twinning associated with the tetragonal form and therefore the degree of strengthening. This
11 is due to the lower thermal expansion of the cubic leucite and loss of the phase transformation
12 and subsequent volume contraction.

13 The fine crystal size and uniformity of microstructure caused by the dispersion of the
14 leucite crystals during heat pressing significantly increases the biaxial flexural strength of the
15 ceramic. Optimization of the microstructure by producing a fine microstructure and controlling
16 its distribution via appropriate pressure parameters is extremely advantageous in these systems.
17 The result is a ceramic material useful in the fabrication of durable aesthetic dental restorations
18 using staining techniques. This technique has the advantage that good aesthetics and contour
19 are maintained without the application of a veneering porcelain which requires longer
20 processing time and incorporates an interface which can be a site for porosity or strength
21 limiting flaws.

22 In a preferred embodiment of the invention, the base frit includes the following:

23 Table 1

24 Glass Composition

Compound	Weight Percent Range
SiO ₂	52.7 - 66
Al ₂ O ₃	6.3 - 18
Li ₂ O	0 - 1.0

1	Na ₂ O	0 - 14.2
2	K ₂ O	4.5 - 31
3	MgO	0 - 1
4	CaO	0 - 3.3
5	SrO	0 - 2.3
6	BaO	0 - 8.1
7	TiO ₂	0 - 3.6
8	B ₂ O ₃	0 - 5.0

9
10 The preparation of the base frit is accomplished by the usual techniques of ceramic
11 fabrication. In a preferred embodiment of the invention the frit is prepared as described in the
12 example below, with exceptions made in the preparation to suit the particular application. Such
13 exceptions include those known by one skilled in the art.

14 In another preferred embodiment, the porcelain has a volume fraction of leucite less
15 than 35%. Even more preferably, the volume fraction is between 20% and 30%.

16
17 **Example**

18 The composition of glass used was as follows:

19 Table 2

20 Glass Composition

21	Compound	Weight Percent
22	SiO ₂	64.9
23	Al ₂ O ₃	16.1
24	K ₂ O	10.9
25	Na ₂ O	4.3
26	CaO	1.7
27	LiO	0.5

TiO ₂	0.4
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These components were transferred to an alumina sagger and heated in an electric furnace and then removed and allowed to air cool. The frit, the product of this process, was ground in an agate ball mill to produce a powder. The powdered frit was then gradually heated to 1120 °C and this temperature was maintained for 45 minutes. After cooling to room temperature the frit was again ground in a ball mill.

The ball milled ceramic powders were measured for the particle size and distribution using a particle analyzer. The ceramic particles were added to a circulating water bath at 37 °C which circulated through a cell and was exposed to a laser, the particle was measured by spherical volume in the range of 1.2 μm to 600 μm.

Experimental frit specimens were produced by weighing 0.96 g of the frit material and mixing with 0.3 ml of distilled water, and transferred to a disc-shaped die, 16 mm in diameter and 50 mm deep. The porcelain slurry was vibrated for 1 minute, tissued for 30 seconds and left under the weight of an inserted plunger for 1 minute. After 30 seconds more of tissueing the specimens were removed and sintered in a porcelain furnace (Multimat MCII™) using the dentine firing cycle listed in Table 4.

Ceramic ingots are then fabricated by dry pressing the frit. A portion of ceramic powder, preferably 2 g, is moistened with three drops of water and transferred to a hardened tool steel die (punch diameter, 12.0 mm). The die punch was loaded with a hydraulic pressure of 74 MPa and held for two minutes. After removal from the die, the powder compact was placed on a refractory tray and fired under vacuum to 1025 °C and held for 1.5 minutes. Pressed specimens were produced by sprueing plexiglass discs and attaching to muffle bases with surrounding paper cylinders. Sixty specimens were invested using Empress™ investment material for the staining technique mixed with 30 ml of special investment and 12 ml of water for 60 seconds and vibrated into the cylinders. Muffle gauges were placed on top of the cylinders to ensure a flat top to all the refractories. Refractories were allowed to set for 1 hour and transferred to a cold burnout furnace (5635 Kavo FWT™) together with alumina plungers

only. Heating proceeded at 3 °C per minute to 890 °C and held for 90 minutes. Cold ceramic ingots were placed into the refractory muffles and a plunger inserted before transferring to a preheated FP500 press furnace (Ivoclar-Vivadent™) or Optimal automatic press furnace (Jeneric Pentron™). Twenty specimens were pressed in the EP500 press furnace at 300,000 Pa and forty specimens in the Optimal automatic press furnace at 500,000 Pa pressure at the following pressing parameters:

Table 3
Pressing Parameters

Start temperature	T1	700 °C
Pressing temperature (high)	T2	1040 °C
Rate of climb	R	40 °C/min*
Vacuum	V	101%
Hold before pressing	H1	20 min
Pressing time	H2	15 min

*A rate of climb of 60 °C/min was selected when processing the Optimal automatic press. All refractories processed in the optimal autopress received a 15 minute air cooling cycle at the end of the pressing cycle automatically delivered by the machine. After cooling, investment was removed from the sample discs with a sandblasting unit using 50 micron glass beads at 300,000 Pa pressure. A diamond disc and a sintered diamond bur removed the sprue areas. The specimens were wet ground with 220, 320, 500, and 800 grade silicon carbide paper mounted on a metallographic lapping machine. Those specimens pressed in the Optimal autopress were lapped as above on one surface only, leaving the tensile surface as sandblasted. Specimens were cleaned using an ultrasonic bath for 10 minutes at 50 °C, followed by washing in detergent and water and a hot water rinse at 50 °C. Specimen dimensions were approximately 14 mm (diameter) x 2 mm (depth). All specimens were fired in a porcelain furnace according to the firing cycles listed in Table 4. These firing cycles were designed to mimic realistic firings necessary to produce dental restorations using the staining technique.

Table 4
Firing Cycles

Firing	Dentine Firing	Stain / Glaze Firing	Strength Glaze Firing
Firing temp. (°C)	1040	780	816
Temp rise (°C/min)	38	55	55
Standby temp. (°C)	538	538	500
Closing time (min)	10	3	7
Holding time (min)	2	0	0.3
Drying time (min)	5	1	5
Preheat (min)	5	2	2
Vacuum (hPa)	55	Nil	Nil
Vacuum off (°C)	1025	Nil	Nil
Cool time (min)	9	3	3

Each specimen was given a Stain / Glaze Firing, a Glaze Firing and a Strength Glaze Firing. The experimental frit was given a Dentine Firing as well.

The piston on three ball test (ASTM Standard F394-78, 1991) was used to flexure test the specimens. The thickness of the specimens was measured centrally and approximately at the three support points using a micrometer and the mean values recorded to the nearest 0.01 mm. The specimen diameters were measured at three equidistant locations around the disc periphery and recorded as previously. Disc specimens were centered and supported on three steel spheres of 3.18 mm diameter, positioned 120 degrees apart on a circle of 10 mm in diameter. A thin plastic sheet was positioned between the specimen surface and the flat ended loading cylinder (1.58 mm diameter) to distribute the load evenly. The specimens were loaded in a universal testing machine with a 30 kn load cell at a cross head speed of 0.15 mm/minute until failure. The recorded fracture load was used in conjunction with the following equation to give the flexural strength.

$$S = 0.2387 P (X-Y)/d^2$$

Where S = flexural strength in (MPa); P = total load causing fracture (N);

$X = (1+\nu) \ln (B/C)^2 + [(1-\nu)/2] (B/C)^2$; $Y = (1+\nu) [1 + \ln (A/C)^2] + (1-\nu) (A/C)^2$; ν = Poisson's ratio (assumed to be 0.25); A=radius of support circle (mm); B=radius of loaded area or ram tip (mm); C= radius of specimen (mm); d= specimen thickness (mm).

Table 5 summarizes the results of these tests.

Table 5
Strength Test Results

Ceramic	No. of tests	Mean Strength (MPa)	Standard Deviation (MPa)	Coefficient of Variation %
Experimental Frit	20	107.2	± 16.4	15.3
Heatpressed Trial 1	20	156.5	± 18.5	11.8
Heatpressed Trial 2	20	160.4	± 19.9	12.4
Heatpressed Trail 3	20	150.0	± 14.7	9.8

The strength data was analyzed using a one way ANOVA (spss ver 6.1) and the results were highly significant (F test, $P=0.0000$). The heat pressed groups, trials 1, 2, and 3 produced the highest biaxial strength values and were significantly different to the sintered specimen when analyzed using the Scheffé F multiple comparison test ($p < 0.05$). There was no statistical difference between strength values for heat pressed groups 1, 2, and 3 ($p > 0.05$). The heat pressed materials also displayed higher probability of failure stress levels and m values than the sintered frit material which was confirmed by the overlap of their confidence intervals at the 95% level. These data are summarized in Table 6.

Table 6

Statistical Analysis of Strength Data

Material	m value	σ 0.01 (MPa)	σ 0.01 (MPa)	σ 0.01 (MPa)	R^2	σ_{no}
Experimental Frit	7.2	60.3	75.6	83.5	0.962	114.0
Heatpressed Trial 1	10.6	106.0	123.7	132.4	0.911	163.7
Heatpressed Trial 2	9.5	103.7	123.2	132.9	0.965	168.6
Heatpressed Trial 3	12.4	107.9	123.1	130.5	0.938	156.4

m value = Weibull modulus

σ 0.01 = Stress levels at 1% probability of failure

σ 0.05 = Stress levels at 5% probability of failure

σ 0.10 = Stress levels at 10% probability of failure

R^2 = Regression coefficient

σ_{no} = Weibull characteristic strength

In order to arrive at this analysis, the double logarithm of $1/(1-\text{median rank})$ was plotted vertically verses the logarithm of the actual data values and a straight line fitted through the points using the median rank regression method (determined by least squares regression curve fitting). Strength levels at the 1%, 5%, and 10% probability of failure were calculated using the Weibull plots. The equation of Weibull two parameter distribution function used is:

$$Pf = 1 - \exp [-(\sigma/\sigma_{no})^m]$$

Where Pf = probability of failure; σ = strength at a given Pf;

σ_{no} = characteristic strength; and m = Weibull modulus

1 Further analysis involved secondary electron imaging of the samples. This was
2 performed by polishing the samples with 1 μm then a 3 μm alumina micropolish and steam
3 cleaned. Cleaning in alcohol for 30 seconds and water rinsing was carried out before ultrasonic
4 cleaning for 1 minutes at 50 °C. Specimen etching was achieved using 0.1% hydrofluoric acid
5 for 1 minute followed by water rinsing. Etched and fractured specimens were mounted on
6 coded brass stubs and gold coated using a sputter coater for 100 seconds at 40 milliamps.
7 Secondary electron imaging was carried out using a field emission scanning electron
8 microscope at a working distance of 15 mm, using an accelerating voltage of 10 kv. One
9 photomicrograph was taken per etched specimen (five per specimen test group) so that the
10 microstructure of the sintered and pressed materials could be quantitatively compared. One
11 specimen per heat pressed groups 1 and 2 was polished as previously and carbon coated to
12 allow elemental analysis of crystalline phases which could not be identified using x-ray
13 diffraction. Energy dispersive X-ray analysis was used on the carbon coated specimens in a
14 scanning electron microscope using 20 kv. Characteristic X-rays were acquired using a
15 pentafer detector and a beryllium window to give quantitative results, via an X-ray analysis
16 program.

17 Analysis of the sintered frit material revealed a dense dispersal of fine leucite crystals
18 ($1.0 \pm 1.2 \mu\text{m}^2$) interspersed between areas of glassy matrix and a mean leucite area fraction
19 of 19.0%. There was virtually no microcracking in the glassy matrix or around the leucite
20 crystals in either the sintered or heat pressed samples examined, with microcracking restricted
21 to the leucite crystals in all the samples examined. The heat pressed ceramic displayed a
22 uniform distribution of fine ($1.2 \pm 1.1 \mu\text{m}^2$) tetragonal leucite crystals evenly dispersed in the
23 glassy matrix and a mean leucite area fraction of 18.0%. Leucite crystal twinning was present
24 in all the materials tested.

25 Finally, X-ray diffraction analysis was performed by taking fractured disc segments
26 randomly from the specimens and grinding them into a powder. The heat pressed group before
27 application of firing cycles and the starting glass before nucleation and growth were also

1 analyzed. The samples were placed in the holder of a diffractometer and using flat plate
2 geometry, data was collected.

3 The X-ray diffraction pattern for the starting frit before nucleation and growth indicates
4 an amorphous glassy phase and some small peaks for titanium dioxide. The powder frit used
5 for the sintered specimens and the pressed material consists of two major solid phases, an
6 amorphous component and tetragonal leucite. Analysis of the pressed ceramic before the firing
7 cycles also produced identical phases.

8 While the invention has been described in conjunction with the specific embodiments
9 outlined above, it is evident that many alternatives, modifications, and variations will be
10 apparent to those skilled in the art. Accordingly, the preferred embodiments of the invention
11 are intended to be illustrative and not limiting. Various changes may be made without departing
12 from the spirit and scope of the invention as defined in the claims.

CLAIMS

We claim:

1. A pressed porcelain having a homogeneous leucite particle distribution.
2. The porcelain of claim 1 wherein said leucite particles are between 0.1 and 2.3 μm in size.
3. The porcelain of claim 1 wherein said leucite particles have a uniform orientation.
4. The porcelain of claim 1 wherein the flexural biaxial strength component of the porcelain exceeds 150 MPa..
5. The porcelain of claim 1 wherein the volume fraction of leucite is less than 35% of the total porcelain volume.
6. The porcelain of claim 5 wherein the volume fraction of leucite is between 20% and 30% of the total porcelain volume.
7. A heat pressed porcelain having a homogeneous leucite particle distribution, made from a base frit comprising, by weight percent:

SiO_2	52.7 - 66;
Al_2O_3	6.3 - 18;
Li_2O	0 - 1.0;
Na_2O	0 - 14.2;
K_2O	4.5 - 31;
MgO	0 - 1;
CaO	0 - 3.3;
SrO	0 - 2.3;
BaO	0 - 8.1;
TiO_2	0 - 3.6;
B_2O_3	0 - 5.0; and
LiO	0 - 0.5.

- 1
2 8. The porcelain of claim 7 wherein said base frit comprises approximately, by weight
3 percent:

4 SiO_2	64.9;
5 Al_2O_3	16.1;
6 LiO	0.5;
7 Na_2O	4.3;
8 K_2O	10.9;
9 CaO	1.7; and
10 TiO_2	0.4.

- 11
12 9. A method for producing a leucite reinforced ceramic comprising the following steps:
13 preparing a glass sample by heating, cooling, and thereafter grinding into a powder;
14 mixing the powder with water;
15 sintering the slurry under pressure.

- 16
17 10. The method of claim 9 wherein the glass sample comprises, by weight percent:

18 SiO_2	52.7 - 66;
19 Al_2O_3	6.3 - 18;
20 Li_2O	0 - 1.0;
21 Na_2O	0 - 14.2;
22 K_2O	4.5 - 31;
23 MgO	0 - 1;
24 CaO	0 - 3.3;
25 SrO	0 - 2.3;
26 BaO	0 - 8.1;
27 TiO_2	0 - 3.6;

1 B_2O_3 0 - 5.0; and
2 LiO 0 - 0.5.
3

4 11. The method of claim 10 wherein the glass sample comprises, by weight percent:

5 SiO_2 64.9;
6 Al_2O_3 16.1;
7 LiO 0.5;
8 Na_2O 4.3;
9 K_2O 10.9;
10 CaO 1.7; and
11 TiO_2 0.4.
12

13 12. A porcelain produced by the method of claim 11.
14

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/04806

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C03C 10/12

US CL : 501/6, 68

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 501/6, 68

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,653,791 A (PANZERA et al) 05 August 1997, see col. 3, lines 28-37.	1-7,9,10
X,P	US 5,944,884 A (PANZERA et al) 31 August 1999, see col. 3, lines 34-43.	1-7,9,10
X	US 5,698,019 A (FRANK et al) 16 December 1997, see column 4, lines 35-38.	1-11
A,P	US 5,994,246 A (DENRY) 30 November 1999.	1-11
A	US 4,798,536 A (KATZ) 17 January 1989.	1-11
X,P	WO 99/18912 A (BRODKIN et al), 22 April 1999, see entire document. <i>↳ Rb - Locat</i>	1-11



Further documents are listed in the continuation of Box C.



See patent family annex.

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Special categories of cited documents:

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document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search

10 MAY 2000

Date of mailing of the international search report

07 JUN 2000

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